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Photophysical Studies of Uranyl Complexes

VIII. Luminescence Spectra of $UO_2SO_4 \cdot 3\frac{1}{2}H_2O$ and Two Polymorphs of Bis(urea) Uranyl Sulfate

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The photoluminescence spectra of hydrated and anhydrous uranyl sulfates have been studied under conditions of high resolution at cryogenic temperatures. All uranyl sulfate systems were found to yield nonequivalent spectra: the energies for the electronic and vibronic origins were found to vary with the system, and certain uranyl vibrational frequencies exhibited a dependence on environment. These differences must reflect the various ways in which the uranyl centers are linked by the bridging sulfate groups, as this linking is the main difference between the various structures. © 1985 Academic Press, Inc.

Introduction

The crystal chemistry associated with uranyl sulfate compounds has been found to be quite variable, and multiple forms for a given salt are commonly noted. The existence of several hydrated salts has been demonstrated, with crystal structures for $UO_2SO_4 \cdot 2\frac{1}{2}H_2O$ (*1*) and $UO_2SO_4 \cdot 3\frac{1}{2}H_2O$ (*2, 3*) having been published. More recently, Toivonen and Niinisto reported that two polymorphs of anhydrous bis(urea) uranyl sulfate could be produced (*4*).

The influence of structural parameters on the spectroscopic properties of the uranyl ion is of importance, and hence we have recently been engaged in using high-resolution luminescence spectroscopy as a means to study the possible correlations. In the present work, we detail the investigations

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into the luminescence spectra of the uranyl ion as obtained within the various sulfate host systems.

Experimental

$UO_2SO_4 \cdot 3\frac{1}{2}H_2O$ was prepared according to the literature method (*3*). The materials were characterized on the basis of their elemental analysis and structural properties. The water content of the hydrated sulfate was verified through thermogravimetric analysis. The samples of the α- and β-bis(urea) uranyl sulfates were taken from the same preparation of material used in the crystal structure determinations, and the syntheses and characterization of these materials is described in this work (*4*).

All spectra were obtained on a high-resolution emission spectrometer constructed at Seton Hall University. Samples were excited by the UV output (typically 50 mW at 350 nm was used) of an Ar-ion laser (Coherent Model Innova 90-5). The emission was analyzed at 1 cm^{-1} resolution by a 1-m grating monochromator (Spex Model 1704), detected by a cooled photomultiplier tube (S-20 response), and processed through the Spex digital photometer. In most work, the sample temperature was held between 8.5 and 9.0°K. The uranyl materials were mounted on a Cu block bolted onto the cold stage of a closed-cycle cryogenic refrigerator system (Lake Shore Cryotronics Model LTS-21).

Results and Discussion

In each system the uranium atom exhibits a pentagonal bipyramidal polyhedron, and the various structures differ mainly in how these polyhedra are linked into infinite chains.

The highest degree of characterization for a hydrated polymorph of uranyl sulfate was reported for the α-form of $UO_2SO_4 \cdot 3\frac{1}{2}H_2O$ (*2, 3*). The crystal class was reported to be monoclinic in the nocentric space group $P2_1\,ca$. The structure is basically that of a dimer in which the uranium atom lies at the center of a pentagonal bipyramidal arrangement of oxygen atoms. Each sulfate anion contributes three oxygen atoms that connect three uranium centers, and the remaining oxygen in the sulfate anion is hydrogen-bonded to a water molecule. Accordingly, the uranium coordination sphere consists of three oxygen atoms from sulfate groups and two oxygen atoms from coordinated water molecules, with the sulfate anions being monodentate with respect to each uranium center.

The two polymorphs of bis(urea) uranyl sulfate exhibit structures that are quite similar to each other (*4*). Each of these was again found to exhibit monoclinic structures, and both fell into the $P2_1/c$ space groups. Again, the uranium atom lies at the center of a pentagonal bipyramid composed solely of oxygen atoms. Three of the oxygen atoms are donated by sulfate groups binding in a monodentate fashion, and two of the oxygen atoms are furnished by urea molecules (also binding in a monodentate fashion). The sulfate groups join the pentagonal bipyramids into infinite double chains much in the same fashion as noted for the hydrated uranyl sulfates.

A. α-$UO_2SO_4 \cdot 3\frac{1}{2}H_2O$

The spectra obtained for the hydrated uranyl sulfate were found to behave in a conventional manner. The cryogenic luminescence consisted of a sequence of four well-separated band systems, with each of these in turn containing a relatively few number of peaks. The band system observed at highest energy (denoted as band system A) was found to differ from those at lower energies, but the second, third, and fourth systems (band systems B, C, and D, respectively) were all found to be exact duplicates of each other. Examples of the luminescence obtained within bands A and B

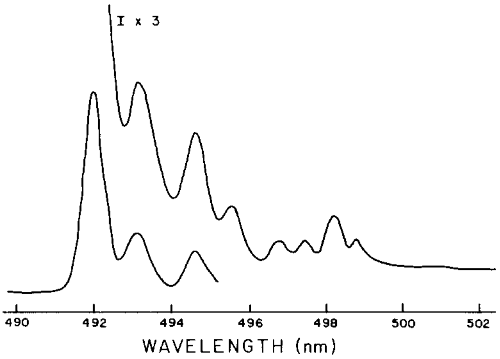

FIG. 1. Luminescence spectrum at 9°K of the electronic origin and the associated vibronic sidebands obtained for α-$UO_2SO_4 \cdot 3\frac{1}{2}\ H_2O$. The spectrum corresponds to band system A as described in the text.

for $UO_2SO_4 \cdot 3\frac{1}{2}H_2O$ are located in Figs. 1 and 2. Survey data obtained at 77°K strongly resembled those of 10°K, and hence we have ruled out the possibility of any low-temperature phase changes, or that the observed luminescence originates from traps or defect centers.

From this information, it may be concluded that all emission takes place out of a single excited state and that only one species is responsible for the luminescence. The electronic origin for the luminescence of $UO_2SO_4 \cdot 3\frac{1}{2}H_2O$ was located at 20,325 cm^{-1}. A vibronic band corresponding to the coupling of the uranyl bending mode with the origin could be observed, with an energy of 253 cm^{-1} being obtained. The remaining peak assignments have been collected in Table I.

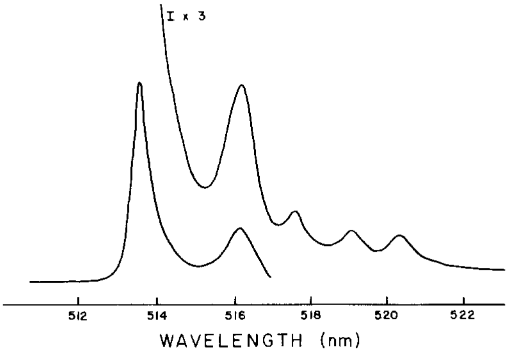

FIG. 2. Luminescence spectrum at 9°K of the highest energy vibroic origin and its associated vibronic structure obtained for α-$UO_2SO_4 \cdot 3\frac{1}{2}\ H_2O$. This spectrum corresponds to band system B.

TABLE I

WAVELENGTHS, ENERGIES, AND ASSIGNMENTS OF THE LUMINESCENCE PEAKS OBSERVED FOR $(UO_2SO_4)_2 \cdot 7H_2O$

Wavelength (Å)	Energy (cm^{-1})	Assignment
	(a) Band system A	
4920	20,325	O–O origin [O]
4931	20,279	O–VL
4946	20,218	O–V1
4954	20,185	O–V2
4970	20,121	O–V3
4975	20,100	O–V4
4982	20,072	O–Vb
4987	20,050	O–V5
	(b) Band system B	
5136	19,469	O–Vs
5162	19,371	O–Vas
5175	19,322	O–Vs–V2
5191	19,265	O–Vs–V3
5203	19,218	O–Vs–Vb
	(c) Band system C	
5372	18,616	O–2 Vs
5399	18,521	O–Vs–Vas
5414	18,470	O–2 Vs–V2
5431	18,413	O–2 Vs–V3
5445	18,366	O–2 Vs–Vb
	(d) Band system D	
5628	17,767	O–3 Vs
5657	17,676	O–2 Vs–Vas
5676	17,618	O–2 Vs–V2
5694	17,561	O–3 Vs–V3
5710	17,514	O–3 Vs–Vb

Notes. Vibrational energies: Vs (totally symmetric uranyl stretch) = 852 cm^{-1}, Vas (antisymmetric uranyl stretch) = 954 cm^{-1}, Vb (uranyl bending mode) = 253 cm^{-1}, (lattice mode) VL = 47 cm^{-1}, (uranyl-sulfate vibrations) V1 = 108 cm^{-1}, V2 = 147 cm^{-1}, V3 = 204 cm^{-1}, V4 = 225 cm^{-1}, and V5 = 275 cm^{-1}.

Bands B, C, and D are known to derive from the coupling of the totally symmetric uranyl stretching mode with the pure electronic origin and vibronic sidebands of band system A. For $UO_2SO_4 \cdot 3\frac{1}{2}H_2O$ it was

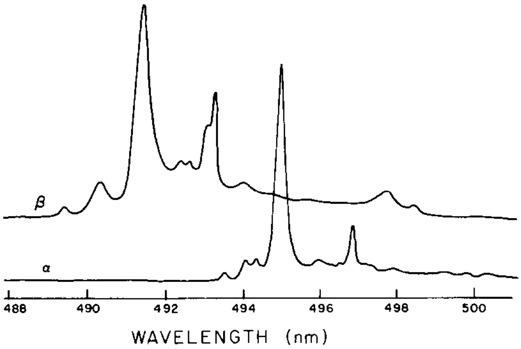

FIG. 3. Luminescence spectrum at 9°K of the electronic origin and the associated vibronic sidebands obtained for the α (lower trace) and β (upper trace) polymorphs of bis(urea) uranyl sulfate. The spectra correspond to band system A as described in the text.

found that v_s = 852 cm^{-1}. Independent confirmation of this value was not possible since one does not normally observe the symmetric stretching mode in the infrared absorption spectrum. Coupling to the antisymmetric uranyl stretching mode was also evident in the luminescence spectra, and an energy of 954 cm^{-1} was deduced for this mode. The antisymmetric mode is observable in the infrared spectra, and a value of 952 cm^{-1} was obtained for this vibrational mode.

The remainder of the peaks observed in the progressions of band systems B, C, and D are assignable to coupling of the symmetric uranyl stretching mode with a few of the vibronic sidebands of band system A. These assignments are also located in Table I.

B. Bis(Urea) Uranyl Sulfates

As noted earlier, exchange of coordinated water for coordinated urea does not result in large changes of the uranyl coordination polyhedron.

However, the spectra obtained for the bis(urea) uranyl sulfates were quite different from each other, and from the hydrated uranyl sulfate. Examples of the spectra obtained within band systems A and B are shown in Figs. 3 and 4 for the two structural polymorphs; the spectra for bands C and D are identical (except for the wavelength shift) with those of band B.

Unlike the situations noted for the hydrated uranyl sulfate, the intensity of the origins located in band A for the α- and β-polymorphs were also found to be quite weak. The energies of the origins were found to differ with the crystal structure: 20,270 cm^{-1} for the α-form and 20,429 cm^{-1} for the β-form. It is worth noting that the origin associated with the luminescence of the hydrated uranyl sulfates lies intermediate between the values for the anhydrous sulfates. Approximately 20 vibronic transitions were noted in the A band systems of the α- and β-forms, although most of these were of rather low intensity.

The energy of the uranyl bending mode normally ranges between 200 and 250 cm^{-1} (5), and a vibronic peak due to coupling with this mode is normally prominant in the spectrum of band system A. For the anhydrous uranyl sulfates, no peak was observed at energy values falling within the acceptable range. However, a strong vibronic peak was observed at much lower energies: 141 cm^{-1} for the α-form and 153 cm^{-1} for the β-form. We have assigned

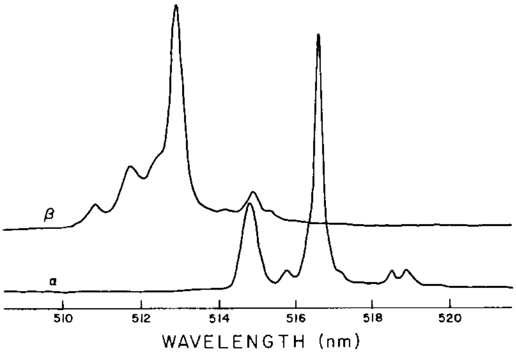

FIG. 4. Luminescence spectrum at 9°K of the highest energy vibronic origin and its associated vibronic structure obtained for the α (lower trace) and β (upper trace) polymorphs of bis(urea) uranyl sulfate. These spectra correspond to band system B.

TABLE II

WAVELENGTHS, ENERGIES, AND ASSIGNMENTS OF THE LUMINESCENCE PEAKS OBSERVED FOR α-BIS(UREA) URANYL SULFATE

Wavelength (Å)	Energy (cm^{-1})	Assignment
(a) Band system A		
4933	20,270	0–0 origin [0]
4940	20,241	0–VL1
4943	20,230	0–VL2
4950	20,202	0–V1
4955	20,182	0–V2
4959	20,165	0–V3
4964	20,144	0–V4
4968	20,129	0–Vb
4970	20,119	0–V5
4973	20,109	0–V6
4979	20,085	0–V7
4988	20,050	0–V8
4991	20,037	0–V9
4996	20,016	0–V10
5002	19,992	0–V11
5013	19,948	0–V12
5017	19,934	0–V13
5021	19,917	0–V14
(b) Band system B		
5147	19,427	0–Vs
5158	19,388	0–Vs–VL2
5166	19,358	0–Vas and 0–Vs–V1
5171	19,339	0–Vs–V2
5185	19,288	0–Vs–Vb
5189	19,273	0–Vs–V5
(c) Band system C		
5382	18,581	0–2 Vs
5395	18,536	0–2 Vs–VL2
5401	18,515	0–Vs–Vas and 0–2 Vs–V1
5408	18,492	0–2 Vs–V2
5420	18,450	0–2 Vs–Vb
5425	18,433	0–2 Vs–V5
(d) Band system D		
5638	17,738	0–3 Vs
5652	17,693	0–3 Vs–V1
5658	17,674	0–2 Vs–Vas and 0–3 Vs–V1
5667	17,646	0–3 Vs–V2
5677	17,615	0–3 Vs–Vb
5683	17,595	0–3 Vs–V5

Notes. Vibrational energies: Vs (totally symmetric uranyl stretch) = 843 cm^{-1}, Vas (antisymmetric uranyl stretch) = 912 cm^{-1}, Vb (uranyl bending mode) = 141 cm^{-1}, (lattice modes) VL1 = 29 cm^{-1} and VL2 = 40 cm^{-1} (uranyl-sulfate vibrations) V1 = 68 cm^{-1}, V2 = 88 cm^{-1}, V3 = 105 cm^{-1}, V4 = 126 cm^{-1}, V5 = 151 cm^{-1}, V6 = 161 cm^{-1}, V7 = 185 cm^{-1}, V8 = 220 cm^{-1}, V9 = 233 cm^{-1}, V10 = 254 cm^{-1}, V11 = 278 cm^{-1}, V12 = 322 cm^{-1}, V13 = 336 cm^{-1}, and V14 = 353 cm^{-1}.

these frequencies to the uranyl bending mode; the only other alternative is that the bending mode does not couple.

Bands B, C, and D derive from the coupling of the totally symmetric uranyl stretching mode with the pure electronic transition and vibronic sidebands of band system A. For α-$UO_2SO_4 \cdot (urea)_2$ it was determined that υ_s = 843 cm^{-1}, and for β-$UO_2SO_4 \cdot (urea)_2$ it was found that υ_s = 853 cm^{-1}. Coupling to the asymmetric stretch-

TABLE III

WAVELENGTHS, ENERGIES, AND ASSIGNMENTS OF THE LUMINESCENCE PEAKS OBSERVED FOR β-BIS(UREA) URANYL SULFATE

Wavelength (Å)	Energy (cm^{-1})	Assignment
(a) Band system A		
4895	20,429	0–0 origin [0]
4905	20,386	0–VL
4914	20,349	0–V1
4924	20,309	0–V3
4927	20,298	0–V4
4931	20,279	0–V5
4933	20,272	0–Vb
4935	20,262	0–V6
4977	20,092	0–V13
4984	20,065	0–V14
(b) Band system B		
5108	19,576	0–Vs
5119	19,536	0–Vas
5129	19,498	0–Vs–V1
5142	19,449	0–Vs–V4
5149	19,421	0–Vs–Vb
5153	19,407	0–Vs–V6
(c) Band system C		
5342	18,720	0–2 Vs
5352	18,685	0–Vs–Vas
5363	18,645	0–2 Vs–V1
5379	18,592	0–2 Vs–V4
5385	18,270	0–2 Vs–Vb
5390	18,553	0–2 Vs–V6
(d) Band system D		
5597	17,868	0–3 Vs
5607	17,834	0–2 Vs–Vas
5619	17,797	0–3 Vs–V1
5636	17,742	0–3 Vs–V4
5643	17,722	0–3 Vs–Vb
5650	17,700	0–3 Vs–V6

Notes. Vibrational energies: Vs (totally symmetric uranyl stretch) = 853 cm^{-1}, Vas (antisymmetric uranyl stretch) = 893 cm^{-1}, Vb (uranyl bending mode) = 153 cm^{-1}, (lattice mode) VL = 43 cm^{-1}, (uranyl-sulfate vibrations) V1 = 78 cm^{-1}, V3 = 118 cm^{-1}, V4 = 129 cm^{-1}, V5 = 149 cm^{-1}, V6 = 167 cm^{-1}, V13 = 335 cm^{-1}, and V14 = 362 cm^{-1}.

ing mode of the uranyl ion was also evident in the luminescence spectra. For the α-form it was found that $\upsilon_{as} = 912\ \text{cm}^{-1}$, and for the β-form $\upsilon_{as} = 893\ \text{cm}^{-1}$. Confirmation of the υ_{as} values was possible from an examination of the infrared absorption spectra. For the α-polymorph a strong absorption at 907 cm^{-1} was found, and for the β-polymorph a band at 898 cm^{-1} was observed. The υ_s band could not be observed in the infrared spectrum. It is interesting to note that while the hydrated uranyl sulfates exhibited similar energies for the totally symmetric uranyl stretching frequencies, the energy of the antisymmetric mode was considerably different. Complete analyses of the luminescence features associated with α-bis(urea) uranyl sulfate are summarized in Table II, while those for the β-polymorph are located in Table III.

The uranium oxygen axial bond lengths of the hydrated uranyl sulfate (*3*) are essentially equal to those reported for the β-polymorph of the anhydrous uranyl sulfate, and measurably shorter than those of the α-form (*4*). At the same time, the equatorial uranium–oxygen bond lengths are essentially equal for all sulfate systems. These observations suggest that the significant spectral differences observed for the uranyl sulfates are not associated with perturbations of the uranyl polyhedron. Since the various structures differ mainly in how the infinite chains are joined, then one must conclude that the spectral variations reflect the various modes of coupling.

These coupling modes do not appear to exert a significant influence on the energies of the totally symmetric uranyl stretching mode. However, much larger effects are noted in comparing the antisymmetric stretching and bending modes. The values for these frequencies were invariably found to be considerably larger for the hydrated uranyl sulfates versus the anhydrous uranyl sulfates. That such differences could be noted for systems of equivalent uranyl polyhedra casts doubt on correlations which have sought to relate uranyl bond lengths with vibrational frequencies (*6*).

Acknowledgments

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